

Comment on the “Novel Isotope Effects Observed in Polarization Echo Experiments in Glasses”

In a recent letter [1], Nagel et al. have conclusively demonstrated that the remarkable, unexpected effect of magnetic field on the low temperature anomalies in some amorphous substances arises from the coupling of the nuclear quadrupole moments (QM) to the residual anharmonic degrees of freedom commonly referred to as the two-level systems (TLS). This was achieved by comparing the dependences of the spontaneous echo decay rate on the magnetic field strength in regular and fully deuterated amorphous glycerol. Quadrupole splitting introduces an additional source of relaxation, thus reducing the echo amplitude by about 50% in the deuterated sample. A magnetic field of sufficient strength restores the signal (see below). But even in regular glycerol some magnetic field effects were observed, albeit weaker in magnitude: about a 3% echo reduction is observed. Based on the natural abundance of the ^{17}O and ^2H isotopes (possessing QM) and assuming that a *single* QM per TLS will account for the effect, Nagel et al. conclude that “on average more than ten glycerol molecules are involved in an individual tunneling process”, subject to the potential presence of other QM carrying impurities. Far from a surprise, this conclusion is expected on theoretical grounds.

We first point out that the TLS are expected to be the low energy limit of multilevel excitations remaining in the liquid after it is quenched below T_g , its glass transition temperature [2]. Such excitations have been predicted to involve about 200 independent molecular units, or “beads”, undergoing strongly anharmonic motions between two alternative local structural states. Tunneling occurs stagewise by moving a “domain wall”, separating those alternative structural states, while individual atoms experience modest displacements of the order the Lindemann ratio $\rho_L \simeq 0.1$ of the bead’s size. At somewhat higher temperatures the domain wall vibrations become thermally activated and give rise to the Boson Peak phenomena [3].

The results of Ref.[1] are quite consistent with this theory. The size of the independently moving units in a liquid can be deduced from the entropy loss upon crystallization, or by detailed fits of the T -dependence of the viscosity above T_g [4]. Using glycerol’s fusion entropy per molecule $\sim 3.5 k_B$ indicates that each molecule of $\text{C}_3\text{H}_8\text{O}_3$ has about 3.5 beads, implying roughly one bead per C-O unit. This is in good accord with chemical intuition. Since the maximum QM induced echo reduction by magnetic field is only $\sim 50\%$, the estimate of the

size of a rearranging region of Nagel at el. should actually be more than 20 glycerol molecules per TLS rather than 10. This lower bound gives about $N_b \sim 70$ beads per tunneling center (TC). We next present two pieces of *direct* evidence of the mesoscopic character of a TC.

The echo “beating” frequency from Fig.3 of Ref.[1], equal to ~ 0.14 MHz, was identified by Nagel et al. as “reflecting directly the mean quadrupole splitting” on a proton site δ_Q , because it is close to the experimentally measured $\delta_Q(\text{C-}^2\text{H})/2\pi = 0.158$ MHz and $\delta_Q(\text{O-}^2\text{H})/2\pi = 0.124$ MHz. On the contrary, the beating frequency should reflect the *total* QM induced splitting Δ_Q of the whole TC, as in the analogous problem of electron spin rotation in radicals with many hyperfine coupled nuclei [5]. Since every bond rotates only about $\rho_L \sim 0.1$ radians during a transition, individual QM contributions to the nutation, $\rho_L \delta_Q$ are small and random; however in deuterated glycerol the number of deuteriums in a TC is large: $N_D \simeq (N_b/3.5) \cdot 8 \simeq 460$, using the theoretical $N_b = 200$. Since the bond rotations are randomly oriented, one gets $\Delta_Q \sim \delta_Q \rho_L \sqrt{N_D}$. The resulting beating frequency is $(\Delta_Q/2)/2\pi \sim 0.14$ MHz! Conversely, associating the beating frequency 0.14 MHz with an *individual* quadrupole splitting would imply a very large angle bond rotation during a tunneling transition.

We stress the difference in echo reduction between normal and deuterated glycerol is not only an effect on the magnitude of the signal. According to Figs. 1 and 2 of Ref.[1], a much weaker field suffices to restore the echo amplitude in the regular sample, a factor of 10 in comparison with the deuterated sample. The echo reduction can be understood as arising from interfering transitions in a large Hilbert space, which is a direct product of the structural transition and the many precessing nuclear spins. The structural states are mixed with the nuclear ones because the electric field gradients are oriented differently in the two structural states. Having *one* QM per TC results in an effective quadrupole splitting of the tunneling center less, by a factor of $N_D^{-1/2}$, than in the deuterated sample because the total “band width” of N random off-diagonal couplings, such as provided by the QM’s, scales as $N^{1/2}$ [7], also consistent with the geometric argument above. The Zeeman splitting on *each* nucleus must exceed this band width by some fixed factor in order to fully energetically separate the distinct nuclear precessions. Assuming ^{17}O and ^2H impurities in regular glycerol contribute equally, the ratio of characteristic fields gives $N_D \sim 3 \cdot 10^2$.

That tunneling centers should involve moving only very few atoms is actually rather unlikely on energetic grounds: Suppose for a moment, in an extreme fashion, that the TC

were indeed very small, i.e. one or two molecular units across. In order to have a *resonant* transition with a reasonable tunneling amplitude, so that it is active at low T , there must be available a “free volume” comparable to the bead’s volume itself. Since the Lindemann ratio is ~ 0.1 at crystallization or vitrification alike, the typical specific volume fluctuations at T_g are about $\sqrt{3} \cdot 0.1$, i.e. 20% or less. Density fluctuations of order 100% have at best $\exp[-(100/20)^2/2] \sim 10^{-6}$ probability! Indeed, point-like defects are rare [6] - at least as rare in glasses as in crystals. The single bead defect density, as estimated above, would be much less than the TLS density needed to explain experiment. Such simplistic, “free-volume” reasoning does not apply to structural transitions encompassing any larger regions, of course, because more complicated motions are allowed thereby that are accompanied by smaller density changes (see details in [4, 8]).

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